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A GENERAL THEORY OF THE SPECTROSCOPIC PROPERTIES
OF PARTIALLY ORDERED ENSEMBLES. II. TWO-VECTOR PROBLEMS

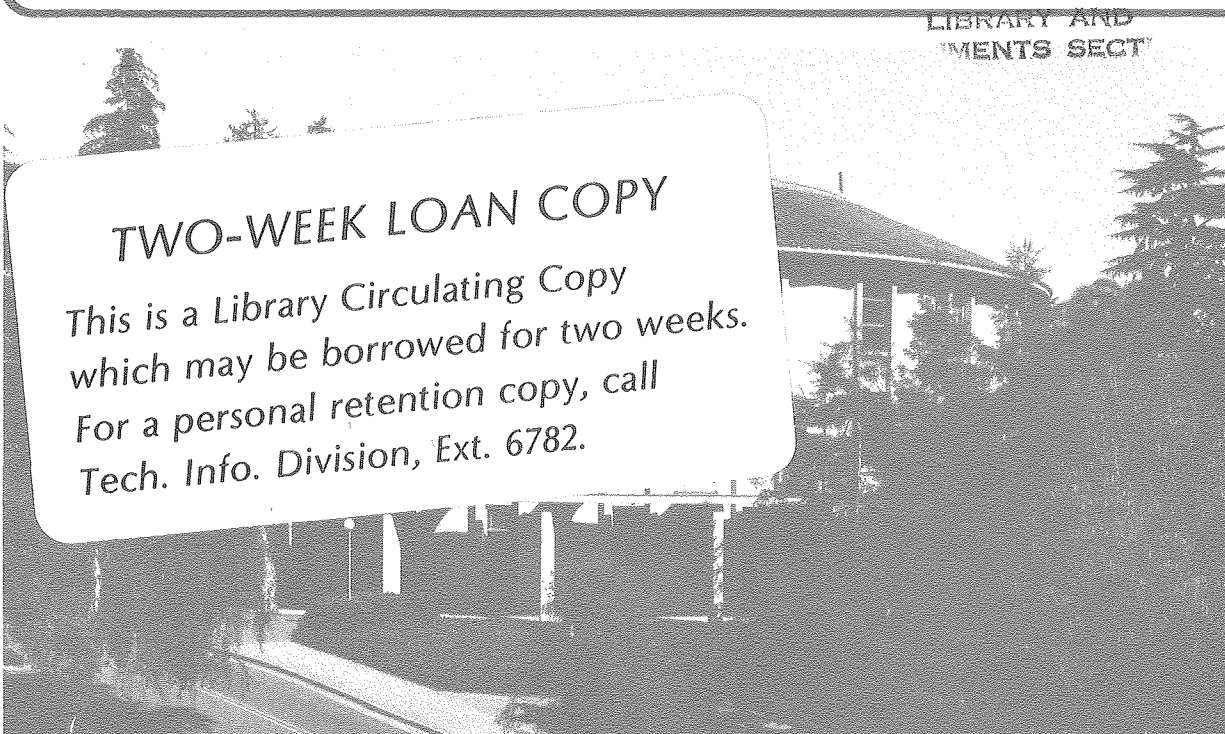John A. Nairn, R. Friesner, and Kenneth Sauer

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A GENERAL THEORY OF THE SPECTROSCOPIC PROPERTIES

OF PARTIALLY ORDERED ENSEMBLES. II.

TWO-VECTOR PROBLEMS.

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ABSTRACT

We have expanded on the results of an earlier paper [J. Chem. Phys. 72, 221 (1980)] which deals with a method for determining the response of a static, partially ordered ensemble of molecules to various types of electromagnetic probes. In this paper we consider types of spectroscopy whose response depends on the location of two vectors in an axis system fixed with respect to the molecule. Examples of such spectroscopies discussed in detail include fluorescence polarization, photoselection linear dichroism, Raman spectroscopy and two-photon absorption. We outline the kinds of structural information available from polarization experiments on partially ordered ensembles.

I.   Introduction

Spectroscopic studies on oriented systems provide impor-
tant sources of structural information in chemical and bio-
logical systems. The problem that we undertake is how to
extract structural information from an observed response
in a partially ordered ensemble. In many cases, the
molecules that comprise the ensemble are spectroscopically
identical and non-interacting. The observed response is,
therefore, a superposition of the responses for the indi-
vidual molecules. The superposition can be calculated by
averaging a response function over an orientational distri-
bution function. In this paper, we will be concerned with
only the static regions in which the molecular motion is
negligible. The orientational averaging will then be done
using a distribution function that is independent of time.

In an earlier paper[1] (hereafter referred to as paper I)
we developed much of the theory involved in calculating
spectroscopic properties of partially ordered ensembles,
and we applied the theory to one-vector problems. One-
vector problems are spectroscopic calculations in which the
response function depends on the orientation of only one
vector in the molecular axis system - i.e., one that is
fixed with respect to the molecule. An example of a one-
vector problem is electron paramagnetic resonance (EPR),
where the signal depends only on the orientation of the
Zeeman field in the molecular axis system. In one-vector

problems, the observed response can be written as

$$\bar{I} = \int\limits_{0}^{\pi} d\theta \int\limits_{0}^{2\pi} d\phi \ D(\theta,\phi,\underset{\sim}{\Delta})I(\theta,\phi) \ d\theta d\phi \qquad (1)$$

where $I(\theta,\phi)$ is the response when the vector of interest has
spherical angles θ and ϕ in the molecular axis system,
$D(\theta,\phi,\underset{\sim}{\Delta})$ is the one-vector density of states function which
gives the probability that the vector of interest has spherical
angles θ and ϕ in the molecular axis system, and $\underset{\sim}{\Delta}$ is a set of
parameters that describe the partial ordering. The chief ad-
vantage afforded by the use of equation (1) in paper I lies in
a formalism, developed earlier,[2] for calculating one-vector
density of states functions from arbitrary models of partially
ordered ensembles. Paper I and reference 2 describe the
details of how to calculate one-vector density of states
functions. Frank et al.[3] and Nairn et al.[4] have applied
the one-vector density of states formalism to obtain structural
information in photosynthetic systems from EPR[3] and linear
dichroism[4] experiments.

The response functions for many spectroscopic properties
are not adequately described by the location of one vector
in the molecular axis system, but depend on the location
of two vectors in the molecular axis system. Examples of
such spectroscopies are fluorescence polarization, photo-
selection linear dichroism, Raman spectroscopy and two photon
absorption. Although the density of states approach was first

used for one-vector problems, it can be extended to include
two-vector problems; this extension is advantageous because
it retains many favorable aspects of the one-vector density
of states techniques.[1-4]

We begin with two unit vectors $\hat{v}_1$ and $\hat{v}_2$ in the
laboratory axis system which are perpendicular to each other
and which define directions of interest. For example, in a
fluorescence polarization experiment, $\hat{v}_1$ could be the
polarization direction of the exciting light and $\hat{v}_2$ could be
the polarization direction of the detected fluorescence. We
now introduce the two-vector density of states function
$P(\theta,\phi,\omega,\underset{\sim}{\Delta})$ which gives the probability that the location
of $\hat{v}_2$ in the molecular axis system is defined by ω when the
spherical angles of $\hat{v}_1$ in the molecular axis system are θ and
ϕ (see fig. 1). The observed response will then be

$$\bar{I} = \int_0^{2\pi} d\omega \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \ I(\theta,\phi,\omega)P(\theta,\phi,\omega,\underset{\sim}{\Delta}) \qquad (2)$$

where $I(\theta,\phi,\omega)$ is the response when $\hat{v}_1$ and $\hat{v}_2$ are defined
by θ,ϕ, and ω in the molecular axis system. As will be shown
in the next section, $P(\theta,\phi,\omega,\underset{\sim}{\Delta})$ can be derived in a manner
that is analogous to the derivation of $D(\theta,\phi,\underset{\sim}{\Delta})$ in reference 2.

Evaluation of $P(\theta,\phi,\omega,\underset{\sim}{\Delta})$ and use of Eq. 2 is sufficient
for analyzing any two-vector problem. We will consider
several examples having the same type of response function,

$$I(\theta,\phi,\omega) = (\hat{v}_2 \cdot \underset{\approx}{T} \cdot \hat{v}_1)^2 \qquad\qquad (3)$$

where $\underset{\approx}{T}$ is a constant tensor in the molecular axis system. We define $\bar{\bar{I}}_\perp$ as the average of a response function like (3). Structural information is obtained by comparing $\bar{\bar{I}}_\perp$ to $\bar{\bar{I}}_\parallel$ where $\bar{\bar{I}}_\parallel$ is the average of the response function

$$I(\theta,\phi) = (\hat{v}_1 \cdot \underset{\approx}{T} \cdot \hat{v}_1)^2 \qquad\qquad (4)$$

Because Eq. (4) is independent of ω, calculation of $\bar{\bar{I}}_\parallel$ is a one-vector problem, and it is evaluated using Eq. (1). Spectroscopies having these response functions include fluorescence polarization, photoselection linear dichroism, Raman spectroscopy, and two-photon absorption.

II. Evaluation of $P(\omega,\theta,\phi,\underset{\sim}{\Delta})$

We follow the same procedure used in ref. 2, where we began with a set of n rotations $R_1(\alpha_1) \ldots R_n(\alpha_n)$ and n weighting functions $g_1(\alpha_1) \ldots g_n(\alpha_n)$ that generate the partially ordered ensemble. The partially ordered ensemble can be thought of as a set of cubes in which the unit vectors in the molecular axis system $(\hat{x}',\hat{y}',\hat{z}')$ lie along the joined edges of the cube. To generate an ensemble by a set of rotations, we begin by placing a cube at the origin of the laboratory axis system (with $\hat{x}'$, $\hat{y}'$, and $\hat{z}'$ coincident with the laboratory axis system unit vectors $\hat{x}$, $\hat{y}$, and $\hat{z}$).

When this cube is rotated by n rotations $[R_1(\alpha_1) \ldots R_n(\alpha_n)]$ in the laboratory frame, it will become a member of the ensemble. Furthermore, the probability that the angular variables are α_1, α_2 ... α_n is given by the product of the weighting functions.

The average intensity for a two-vector problem can be written directly as an integral of the variables $\alpha_1 \ldots \alpha_n$

$$\bar{I} = \frac{1}{N} \int_{\alpha_1} \ldots \int_{\alpha_n} I[\hat{v}_1'(\alpha_1 \ldots \alpha_n), \hat{v}_2'(\alpha_1 \ldots \alpha_n)]$$

$$\times \quad g_1(\alpha_1) \ldots g_n(\alpha_n) \, d\alpha_1 \ldots d\alpha_n \tag{5}$$

where N is a normalization constant, $I[\hat{v}_1'(\alpha_1 \ldots \alpha_n), \hat{v}_2'(\alpha_1 \ldots \alpha_n)]$ is the two-vector response function, and $\hat{v}_1'$ and $\hat{v}_2'$ are the two vectors of interest in the molecular axis system. From ref. 2, the two vectors are

$$\hat{v}_1' = R_1(\alpha_1) \ldots R_n(\alpha_n) \hat{v}_1 \tag{6}$$

$$\hat{v}_2' = R_1(\alpha_1) \ldots R_n(\alpha_n) \hat{v}_n \tag{7}$$

where $\hat{v}_1$ and $\hat{v}_2$ are the two vectors in the laboratory axis system.

The two-vector density of states function $P(\theta,\phi,\omega,\underset{\sim}{\Delta})$ describes the probability that $\hat{v}'_1$ has spherical angles θ and ϕ, and $\hat{v}'_2$ is described by the angle ω defined in fig. 1; in other words, the probability that

$$\hat{v}'_1 = (\cos\phi\sin\theta, \sin\phi\sin\theta, \cos\theta) \tag{8}$$

and

$$\hat{v}'_2 = \begin{pmatrix} \cos\phi\cos\theta\cos\omega + \sin\phi\sin\omega \\ \sin\phi\cos\theta\cos\omega - \cos\phi\sin\omega \\ -\sin\theta\cos\omega \end{pmatrix} \tag{9}$$

We thus perform the transformation

$$(\alpha_1 \ldots \alpha_n) \leftrightarrow (\phi, v_1 \ldots v_{n-3}, \theta, \omega) \tag{10}$$

under the constraints

$$v'_{1x} = \sin\theta\cos\phi$$

$$v'_{1y} = \sin\theta\sin\phi$$

$$v'_{1z} = \cos\theta$$

$$\tag{11}$$

$$v'_{2x} = \cos\phi\cos\theta\cos\omega + \sin\phi\sin\theta$$

$$v'_{2y} = \sin\phi\cos\theta\cos\omega - \cos\phi\sin\omega$$

$$v'_{2z} = -\sin\theta\cos\omega$$

Application of the n dimensional change of variable theorem to equation (5) yields

$$\bar{I} = \frac{1}{N} \int_0^\pi d\theta \int_0^{2\pi} d\phi \int_0^{2\pi} d\omega \; I[\hat{v}_1'(\theta,\phi),\hat{v}_2'(\theta,\phi,\omega)]$$

$$\int_{v_1}\cdots\int_{v_{n-3}} \; \prod_{i=1}^{n} g_i[\alpha_i(\phi,v_1\cdots v_{n-3},\theta,\omega)]$$

$$\left|\frac{\partial \alpha_1\cdots\alpha_n}{\partial\phi,v_1\cdots v_{n-3},\theta,\omega}\right| \; dv_1\cdots dv_{n-3} \qquad (12)$$

where $(\partial\alpha_1\cdots\alpha_n/\partial\phi,v_1\cdots v_{n-3},\theta,\omega)$ is the Jacobian of the coordinate transformation. By inspection we set

$$P(\theta,\phi,\omega,\underset{\sim}{\Delta}) = \frac{1}{N} \int_{v_1}\cdots\int_{v_{n-3}} \; \prod_{i=1}^{n} g_i[\alpha_i(\phi,v_1\cdots v_{n-3},\theta,\omega)]$$

$$\times \left|\frac{\partial\alpha_1\cdots\alpha_n}{\partial\phi,v_1\cdots v_{n-3},\theta,\omega}\right| \; dv_1\cdots dv_{n-3} \qquad (13)$$

Following the approach of reference 2, we pick the laboratory z axis to be the axis of the first rotation $[R_1(\alpha_1)]$, and we use the following transformation

$$\alpha_1 = f_1(\phi,v_1\cdots v_{n-3},\theta,\omega)$$

$$\alpha_2 = v_1$$

$$\circ$$

$$\circ \qquad\qquad (14)$$

$$\circ$$

$$\alpha_{n-2} = v_{n-3}$$

$$\alpha_{n-1} = f_2(v_1\cdots v_{n-3},\theta,\omega)$$

$$\alpha_n = f_3(v_1\cdots v_{n-3},\theta,\omega)$$

where α_{n-1} and α_n are defined by solving the two equations

$$\cos\theta = v'_{1z}(\alpha_2\ldots\alpha_n) \tag{15}$$

$$-\sin\theta\cos\omega = v'_{2z}(\alpha_2\ldots\alpha_n) \tag{16}$$

for α_n and α_{n-1} and setting $\alpha_2\ldots\alpha_{n-2}$ equal to $v_1\ldots v_{n-3}$.
As shown in ref. 2, under the above transformation

$$\alpha_1 = -\phi + f_4(v_1\ldots v_{n-3},\theta,\omega) \tag{17}$$

$$\frac{\partial\alpha_1}{\partial\phi} = -1 \tag{18}$$

and

$$\frac{\partial\alpha_i}{\partial\phi} = 0 \qquad i \neq 1 \tag{19}$$

From equations (17), (18), and (19), the Jacobian simplifies to

$$|J| = \left| \frac{\partial\alpha_{n-1}}{\partial\theta}\frac{\partial\alpha_n}{\partial\omega} - \frac{\partial\alpha_{n-1}}{\partial\omega}\frac{\partial\alpha_n}{\partial\theta} \right| \tag{20}$$

By differentiating both sides of Eq. (15) and Eq. (16) with respect to both θ and ω, we get four equations in the four unknowns $\partial\alpha_{n-1}/\partial\theta$, $\partial\alpha_n/\partial\omega$, $\partial\alpha_{n-1}/\partial\omega$, $\partial\alpha_n/\partial\theta$. Solving these equations for the Jacobian yields

$$|J| = \frac{\sin^2\theta\sin\omega}{\left| \dfrac{\partial v'_{1z}(\alpha_2\ldots\alpha_n)}{\partial\alpha_{n-1}}\dfrac{\partial v'_{2z}(\alpha_2\ldots\alpha_n)}{\partial\alpha_n} - \dfrac{\partial v'_{1z}(\alpha_2\ldots\alpha_n)}{\partial\alpha_n}\dfrac{\partial v'_{2z}(\alpha_2\ldots\alpha_n)}{\partial\alpha_{n-1}} \right|} \tag{21}$$

with $\alpha_2 \ldots \alpha_n$ replaced by their transformed variables $v_1 \ldots v_{n-3}$, $f_2(v_1 \ldots v_{n-3}, \theta, \omega)$, and $f_3(v_1 \ldots v_{n-3}, \theta, \omega)$. Substitution into equation (13) yields

$$P(\theta, \phi, \omega, \underset{\sim}{\Delta}) = \frac{\sin^2\theta \sin\omega}{N} \int_{v_1} \cdots \int_{v_{n-3}} g_1[-\phi + f_4(v_1 \ldots v_{n-3}, \theta, \omega)]$$

$$\times \, g_{n-1}[f_2(v_1 \ldots v_{n-3}, \theta, \omega)] \, g_n[f_3(v_1 \ldots v_{n-3}, \theta, \omega)]$$

$$\times \, \frac{\prod\limits_{i=2}^{n-2} g_i(v_{i-1}) \, dv_{i-1}}{\left| \dfrac{\partial v'_{1z}}{\partial \alpha_{n-1}} \dfrac{\partial v'_{2z}}{\partial \alpha_n} - \dfrac{\partial v'_{1z}}{\partial \alpha_n} \dfrac{\partial v'_{2z}}{\partial \alpha_{n-1}} \right|} \tag{22}$$

Equation (22) is the two-vector density of states function, and it is an extension of equation (31) in ref. 2 for the one-vector density of states function. We note that if $g_1(\alpha_1) = 1$, we have an axially symmetric distribution; i.e. $P(\theta, \phi, \omega, \underset{\sim}{\Delta})$ is independent of ϕ. If we have a randomly oriented system, it can be shown that $P(\theta, \phi, \omega, \underset{\sim}{\Delta}) = $ constant $\times \sin\theta$.

When the partially ordered ensemble can be generated with three rotations, there is no need for the dummy variables $v_1 \ldots v_{n-3}$ in Eq. (14), and hence Eq. (22) will not involve any integration. In such a case, Eq. (22) can be shown to simplify to

$$P(\theta, \phi, \omega, \underset{\sim}{\Delta}) = \sin\theta \; G[\alpha_1(\theta, \phi, \omega), \alpha_2(\theta, \omega), \alpha_3(\theta, \omega)] \tag{23}$$

where $G(\alpha_1, \alpha_2, \alpha_3)$ is the product of the weighting functions

for the three rotations. The two-vector density of states is thus determined by finding the functional form of $\alpha_1(\theta,\phi,\omega)$, $\alpha_2(\theta,\omega)$, and $\alpha_3(\theta,\omega)$. These functional forms for all possible three-rotation schemes and combinations of $\hat{v}_1$ and $\hat{v}_2$ are listed in table I. We do not include $\alpha_1(\theta,\phi,\omega)$, and therefore table I is restricted to axially symmetric two-vector densities of states.

In the remainder of this paper, we will not be concerned with the specific form of $P(\theta,\phi,\omega,\underset{\sim}{\Delta})$, but instead will consider the type of structural information available in two-vector spectroscopy.

III. A Particular Response Function

We will now calculate $\bar{\bar{I}}_\parallel$ and $\bar{\bar{I}}_\perp$ when the response functions are given by Eq. (4) and Eq. (3), respectively. We will restrict our consideration to the case where $P(\theta,\omega,\underset{\sim}{\Delta})$ is axially symmetric; that is, the case where the two-vector density of states function is independent of ϕ. The restriction to axial symmetry is not so limiting as it might seem, because the density of states is axially symmetric in some systems even when the distribution function in the laboratory reference frame is not axially symmetric.[4]

For $\bar{\bar{I}}_\parallel$, we have a one-vector problem; application of equation (1) yields

$$\bar{\bar{I}}_\parallel = \int_0^\pi d\theta \int_0^{2\pi} d\phi \; (\hat{v}_1' \cdot \underset{\approx}{T} \cdot \hat{v}_1')^2 D(\theta,\underset{\sim}{\Delta}) \tag{24}$$

where $D(\theta, \underset{\sim}{\Delta})$ is the one-vector density of states function for θ'_1, θ'_1 is given by equation (8), and

$$\underset{\approx}{T} = \begin{pmatrix} T_{xx} & T_{xy} & T_{xz} \\ T_{yx} & T_{yy} & T_{yz} \\ T_{zx} & T_{zy} & T_{zz} \end{pmatrix} \tag{25}$$

is a constant tensor in the molecular axis system.

Experimentally, partial ordering is induced by exerting some type of force on the system, such as an external alignment field or a mechanical stretch. Because the sign of the direction of these forces is arbitrary, $D(\theta)$ is is symmetric about $\pi/2$; that is, $D(\theta) = D(\pi-\theta)$. Utilizing this symmetry property, expanding equation (24) and evaluating the integral over ϕ results in

$$\bar{I} = \frac{1}{8}\{8T_{zz}^2 + \alpha[8T_{xx}T_{zz} + 4(T_{xz}+T_{zx})^2 + 8(T_{yy}T_{zz})$$

$$+ 4(T_{yz}+T_{zy})^2 - 16T_{zz}{}^2] + \beta[3T_{xx}^2 + 3T_{yy}^2 + 2T_{xx}T_{yy}$$

$$+ (T_{xy}+T_{yx})^2 - 8T_{xx}T_{zz} - 4(T_{xz}+T_{zx})^2 - 8T_{yy}T_{zz}$$

$$- 4(T_{yz}+T_{zy})^2 + 8T_{zz}^2]\} \tag{26}$$

where

$$\alpha = \int_0^{\pi/2} \sin^2\theta \; D(\theta) \; d\theta \tag{27}$$

$$\beta = \int_0^{\pi/2} \sin^4\theta \; D(\theta) \; d\theta \tag{28}$$

and $D(\theta)$ is normalized such that

$$\int_0^{\pi/2} D(\theta) \; d\theta = 1 \tag{29}$$

For $\bar{I}_1$, we require the use of $P(\theta,\omega,\underset{\sim}{\Delta})$; the result is

$$\bar{I} = \int_0^\pi d\theta \int_0^{2\pi} d\phi \int_0^{2\pi} d\omega\, P(\theta,\omega,\underset{\sim}{\Delta})(\hat{v}_2' \cdot \underset{\approx}{T} \cdot \hat{v}_1')^2 \qquad (30)$$

$P(\theta,\omega,\underset{\sim}{\Delta})$ is the two-vector density of states for $\hat{v}_1'$ and $\hat{v}_2'$ where $\hat{v}_1'$ and $\hat{v}_2'$ are given by Eq. (8) and Eq. (9), respectively, and $\underset{\approx}{T}$ is given by Eq. (25). Expanding equation (30) and evaluating the integral over ϕ yields

$$\begin{aligned}
\bar{I}_1 = \frac{1}{8}\{&4(T_{xz}^2+T_{yz}^2) + \alpha[4(T_{xy}^2+T_{yx}^2-T_{xz}^2-T_{yz}^2) - (T_{xy}+T_{yx})^2 \\
&+ (T_{xx}-T_{yy})^2] + \gamma[4(T_{xx}-T_{zz})^2 + 4(T_{yy}-T_{zz})^2 \\
&- 2(T_{xx}-T_{yy})^2 + 2(T_{xy}+T_{yx})^2 - 4(2T_{xz}T_{zx} + 2T_{yz}T_{zy} \\
&+ T_{xy}^2 + T_{yx}^2 + T_{xz}^2 + T_{yz}^2)] + \xi[4(T_{xz}+T_{zx})^2 + \\
&4(T_{yz}+T_{zy})^2 - (T_{xy}+T_{yx}) + (T_{xx}-T_{yy})^2 \\
&- 4(T_{xx}-T_{zz})^2 - 4(T_{yy}-T_{zz})^2]\}
\end{aligned} \qquad (31)$$

where α is, as before,

$$\gamma = \int_0^{\pi/2} d\theta \int_0^{\pi/2} d\omega\, \sin^2\theta\cos^2\omega\, P(\theta,\omega,\underset{\sim}{\Delta}) \qquad (32)$$

$$\xi = \int_0^{\pi/2} d\theta \int_0^{\pi/2} d\omega\, \sin^4\theta\cos^2\omega\, P(\theta,\omega,\underset{\sim}{\Delta}) \qquad (33)$$

and $P(\theta,\omega,\underset{\sim}{\Delta})$ is normalized such that

$$\int_0^{\pi/2} d\theta \int_0^{\pi/2} d\omega\, P(\theta,\omega,\underset{\sim}{\Delta}) = 1 \qquad (34)$$

Eqs. (26) and (31) are valid for any partially ordered system in which the density of states functions are axially symmetric. We will now consider some special cases. In a random ensemble $D(\theta) = \sin\theta$, and $P(\theta,\omega) = \frac{2}{\pi} \sin\theta$; the parameters α, β, γ, and ξ become $\frac{2}{3}$, $\frac{8}{15}$, $\frac{1}{3}$, and $\frac{4}{15}$, respectively. Substitution into equations (26) and (31) yields

$$\bar{I}_{\parallel} = \frac{K}{45}[45A^2 + 4B^2 + 3(T_{xz}+T_{zx})^2 + 3(T_{yz}+T_{zy})^2$$

$$+ 3(T_{xy}+T_{yx})^2] \qquad (35)$$

and

$$\bar{I}_{\perp} = \frac{K}{15}[B^2 + 2(T_{xy}^2 + T_{yx}^2 + T_{xz}^2 + T_{zx}^2 + T_{yz}^2 + T_{zy}^2)$$

$$- (T_{xy}T_{yx} + T_{xz}T_{zx} + T_{yz}T_{zy})] \qquad (36)$$

where

$$A = \frac{1}{3}(T_{xx} + T_{yy} + T_{zz}) \qquad (37)$$

and

$$B^2 = \frac{1}{2}[(T_{xx}-T_{yy})^2 + (T_{yy}-T_{zz})^2 + (T_{xx}-T_{zz})^2] \qquad (38)$$

We will return to the significance of these equations in the next section.

One type of axially symmetric, perfectly ordered system is one where the z axis of each of the molecular axis systems is coincident with the z axis of the laboratory axis system, and all orientations that are rotations about the z axis are equally likely. If spectroscopic

measurements are made with $\hat{V}_1$ along the z axis, then $D(\theta)$ = $\delta(\theta)$ and $P(\theta,\omega) = \frac{2}{\pi}\,\delta(\theta)$, which means $\alpha=\beta=\gamma=\xi=0$. Eqs. (28) and (38) lead to the expected results

$$\bar{\bar{I}}_{\parallel} = T^2_{zz} \tag{39}$$

and

$$\bar{\bar{I}}_{\perp} = \frac{1}{2}(T^2_{xz} + T^2_{yz}) \tag{40}$$

In other words $\bar{\bar{I}}_{\parallel}$ is equal to $(\hat{z}\cdot\underset{\approx}{T}\cdot\hat{z})^2$ and $\bar{\bar{I}}_{\perp}$ is equal to the average of $(\hat{x}\cdot\underset{\approx}{T}\cdot\hat{z})^2$ and $(\hat{y}\cdot\underset{\approx}{T}\cdot\hat{z})^2$.

IV   Examples

A.   Fluorescence Polarization

Fluorescence polarization experiments are typically done with the configuration shown in Fig. 2; a sample is excited with light polarized in the z direction and propagating along the y axis and fluorescence is detected along the x axis, with an analyzing polarizer oriented either along the z axis (F_{zz}) or the y axis (F_{zy}). We let $D(\theta)$ be the one-vector density of states for a unit vector along the laboratory z axis, and $P(\theta,\omega)$ be the two-vector density of states for two unit vectors along the laboratory z axis and the laboratory x axis. Then

$$F_{zz} = \bar{\bar{I}}_{\parallel} \tag{41}$$

and

$$F_{zy} = \bar{\bar{I}}_{\perp} \tag{42}$$

In the dipole approximation, the response function for fluorescence polarization in a static noninteracting ensemble of molecules is

$$I(\theta, \phi, \omega) = K^2(\hat{\mu}_1 \cdot \hat{v}_1')^2(\hat{\mu}_2 \cdot \hat{v}_2')^2 \tag{43}$$

where $\hat{\mu}_1$ is a unit vector along the absorption dipole moment, $\hat{\mu}_2$ is a unit vector along the emission dipole moment, $\hat{v}_1'$ is the polarization direction of the exciting light, $\hat{v}_2'$ is the polarization direction of the detected fluorescence, and K^2 is a constant. Eq. (43) is identical to Eq. (4) when $\underset{\approx}{T}$ is given by the dyad

$$\underset{\approx}{T} = K\hat{\mu}_2 : \hat{\mu}_1 = K\begin{pmatrix} x_2 \\ y_2 \\ z_2 \end{pmatrix} (x_1 \ y_1 \ z_1) = \begin{pmatrix} x_1 x_2 & y_1 x_2 & z_1 x_2 \\ x_1 y_2 & y_1 y_2 & z_1 y_2 \\ x_1 z_2 & y_1 z_2 & z_1 z_2 \end{pmatrix} \tag{44}$$

After incorporation of the elements of $\underset{\approx}{T}$ into Eq's (26) and (31) and some rearrangement, we arrive at

$$F_{zz} = \bar{I}_\| = \frac{K}{8}[8z_1^2 z_2^2 + 4\alpha(z_1^2 + z_2^2 - 10z_1^2 z_2^2 + 4z_1 z_2 \cos\epsilon)$$

$$+ \beta(-5z_1^2 - 5z_2^2 + 35z_1^2 z_2^2 - 20z_1 z_2 \cos\epsilon + 2\cos^2\epsilon + 1)] \tag{45}$$

and

$$F_{zy} = \bar{I}_\perp = \frac{K}{8}[(4z_1^2 - 4z_1^2 z_2^2) + \alpha(3 - 2\cos^2\epsilon - 7z_1^2 - 3z_2^2$$

$$+ 5z_1^2 z_2^2 + 4z_1 z_2 \cos\epsilon) + \gamma(4\cos^2\epsilon - 2z_1^2 + 2z_2^2 - 2$$

$$+ 30z_1^2 z_2^2 - 24z_1 z_2 \cos\epsilon) + \xi(5z_1^2 + 5z_2^2 - 35z_1^2 z_2^2 - 1$$

$$- 2\cos^2\epsilon + 20z_1 z_2 \cos\epsilon)] \tag{46}$$

where ε is the angle between $\hat{\mu}_1$ and $\hat{\mu}_2$. The constant K can be eliminated by calculating the fluorescence polarization, defined as

$$P = \frac{F_{zz} - F_{zy}}{F_{zz} + F_{zy}} \qquad (47)$$

We are left with the three parameters: 1) z_1^2, the angle between the absorption dipole moment and the z axis of the molecular axis system; 2) z_2^2, the angle between the fluorescence dipole moment and the z axis of the molecular axis system; 3) ε, which is the angle between $\hat{\mu}_1$ and $\hat{\mu}_2$. These are the structural parameters that can, in principle, be determined by fluorescence polarization on a partially ordered system.

In the past, most fluorescence polarization experiments have been done on random samples. In such samples, Eqs. (45) - (47) reduce to

$$P = \frac{3\cos^2\varepsilon - 1}{\cos^2\varepsilon + 3} \qquad (48)$$

Only one structural parameter is obtainable from a random sample experiment, while three structural parameters are obtainable from an ordered sample experiment. At first glance, it appears that it would be hopeless to try to extract three numbers from the one measured quantity in Eq. (47). We note, however, that in an ordered system, the $\hat{z}$ direction and the $\hat{x}$ direction will not be equivalent (unless the y axis is an axis of symmetry in the laboratory axis system), which means that new information can be obtained by exciting with light polarized along the $\hat{x}$ axis and measuring

F_{xz} and F_{xy} (see Fig. 3). In a partially ordered sample $F_{zz} \neq F_{zy} \neq F_{xz} \neq F_{xy}$ we, thus, have four measured quantities, or three polarization ratios, as handles on the three structural parameters. This fact contrasts with the random solution where $F_{zz} \neq F_{zy} = F_{xz} = F_{xy}$ and there are only two measured quantities, or one polarization ratio as a handle to the one structural parameter.

B.   Photoselection Linear Dichroism.

In a photoselection linear dichroism experiment, one excites a sample with polarized light and probes an induced absorption change with light polarized either parallel or perpendicular to the exciting light.[5] The response function is

$$I(\theta,\phi,\omega) = K^2 (\hat{\mu}_1 \cdot \hat{\nu}_1')^2 (\hat{\mu}_2 \cdot \hat{\nu}_2')^2 \qquad (49)$$

where $\hat{\mu}_1$ is the absorption dipole moment that is being excited by light polarized along $\hat{\nu}_1'$ and $\hat{\mu}_2$ is the absorption dipole moment that is being probed by light polarized along $\hat{\nu}_2'$. Because Eq. (49) is identical with the response function for fluorescence polarization, everything that applies to fluorescence polarization also applies to photoselection linear dichroism.

C. Raman Spectroscopy

Polarization experiments in Raman spectroscopy are done by exciting along the y axis with light polarized along the z or x axes and detecting scattered intensity along the x axis with an analyzing polarizer oriented along the z or y axes. Analogously to fluorescence polarization experiments, one can measure four quantities, I_{zz}, I_{zy}, I_{xz}, and I_{xy}. Depolarization ratios for a Raman band are derivable from these four quantities.

The intensity scattered in the x direction is given by[6]

$$I = \frac{(\omega - \omega_0)^4}{c^4} I_0 (\hat{v}_2' \cdot \underset{\approx}{T} \cdot \hat{v}_1')^2 \tag{50}$$

where ω and ω_0 are the scattered and incident frequencies, c is the speed of light, I_0 is the incident intensity, $\hat{v}_1'$ and $\hat{v}_2'$ are the polarization directions for the incident and scattered light and $\underset{\approx}{T}$ is the scattering tensor. The elements of the scattering tensor for a transition from vibronic state m to vibronic state n are

$$T_{ij} = (\alpha_{ij})_{mn} = \frac{1}{\hbar} \sum_r [\frac{(M_i)_{rn}(M_j)_{mr}}{\omega_{rm} - \omega_0} + \frac{(M_i)_{mr}(M_j)_{rn}}{\omega_{rn} + \omega_0}] \tag{51}$$

where i and j can be x, y, or z; $2\pi\hbar$ is Planck's constant and the sum is over vibronic states of the molecule. Here, $(M_i)_{rn}$, $(M_j)_{mr}$, etc., refer to the components of the transition moments between vibronic levels and ω_{rm} and ω_{rn} are

frequencies obtained from the energy differences of the vibronic states.[7] The four quantities I_{zz}, I_{zy}, I_{xz}, and I_{xy} can be found (with T_{ij}'s as parameters) by use of Eq. (26) or Eq. (31). For example, $I_{zz} = \bar{\bar{I}}_{\parallel}$ when $D(\theta)$ is the one-vector density of states for a unit vector along the z axis, $I_{xz} = \bar{\bar{I}}_{\perp}$ when $D(\theta)$ is the one-vector density of states for a unit vector along the x axis and $P(\theta,\omega)$ is the two-vector density of states for a unit vector along the x axis, and a unit vector along the z axis, and similarly for I_{zy} and I_{xy}. In this section, we will consider only symmetric scattering tensors; it is then possible to find an axis system, the principal axis system, where $\underset{\sim}{\alpha}_{mn}$ is diagonal with diagonal elements α_x, α_y and α_z. Now, Eq. (26) and Eq. (31) were derived by orientation averaging in a molecular axis system which in general is not the same as the principal axis system. This approach is necessary because, even though the density of states is axially symmetric in some molecular axis system, it may not be axially symmetric in the principal axis system.[2] We can find $\underset{\sim}{I}$ in the molecular axis system by

$$
\underset{\approx}{T} = \underset{\approx}{R}(\Theta,\Phi,\Psi) \begin{pmatrix} \alpha_x & 0 & 0 \\ 0 & \alpha_y & 0 \\ 0 & 0 & \alpha_z \end{pmatrix} \underset{\approx}{R}^{-1}(\Theta,\Phi,\Psi) \tag{52}
$$

or

$$
T_{ij} = \sum_k R_{ik}(\Theta,\Phi,\Psi) R_{jk}(\Theta,\Phi,\Psi) \alpha_k \tag{53}
$$

where k = x,y, and z, and $R(\Theta,\Phi,\Psi)$ is the Euler rotation
matrix with Euler angles Θ,Φ, and Ψ.[8] Because both the princi-
pal axis system and the molecular axis system are fixed with
respect to the molecule, Θ,Φ, and Ψ are constants that are
the same for every member of the ensemble. We now see that
there are six parameters inherent in a Raman experiment; those
six are the three principal components of the scattering
tensor and the three Euler angles that relate the principal
axis system to the molecular axis system.

In a partially ordered sample, one can measure the four
quantities I_{zz}, I_{zy}, I_{xz}, and I_{xy} from which can be constructed
three depolarization ratios. These three ratios are all that
is available to extract the six structural parameters mentioned
above. Although the ratio of parameters to data points is
unfavorable, in some cases a few of the parameters may be
known. For example if the three Euler angles are known from
other experiments, one would have three measured quantities
to determine the three principal components of the scattering
tensor and vice versa.

In a random sample $I_{zz} = \bar{\bar{I}}_{\parallel}$ in Eq. (35) and $I_{zy} = I_{xz}$
$= I_{xy} = \bar{\bar{I}}_{\perp}$ in Eq. (36), which results in only one possible
depolarization ratio. The depolarization ratio is frequently
reported as

$$P = \frac{I_{xz} + I_{xy}}{I_{zz} + I_{zy}} \qquad (54)$$

which, for symmetric tensors   is equal to

$$P = \frac{6[B^2 + 3(T_{xy}^2 + T_{xz}^2 + T_{yz}^2)]}{45A^2 + 7[B^2 + 3(T_{xy}^2 + T_{xz}^2 + T_{yz}^2)]} \qquad (55)$$

A is equal to 1/3 times the trace of $\underset{\approx}{T}$; because the trace is invariant to rotation, A is also equal to $\frac{1}{3}(\alpha_x + \alpha_y + \alpha_z)$. This quantity is known as the spherical part of the polarizibility.[6] In a similar fashion, the quantity $C^2 = B^2 + 3(T_{xy}^2 + T_{xz}^2 + T_{yz}^2)$ can be shown to be also invariant to rotations. In the principal axis system $C^2 = \frac{1}{2}[(\alpha_y - \alpha_x)^2 + (\alpha_y - \alpha_z)^2 + (\alpha_z - \alpha_x)^2]$; this quantity is known as the anisotropy of the polarizability.[6] Eq. (55) reduces to the classical result for the depolarization ratio

$$P = \frac{6C^2}{45A^2 + 7C^2} \qquad (56)$$

Most Raman depolarization measurements have been done on random samples, but for two reasons it is worth undertaking depolarization measurements on ordered samples: 1) It is not possible to obtain structural information (e.g. the Euler angles in Eqs. (51) - (52) through measurements on a random sample; 2) If the Euler angles in Eqs. (51) - (52) are known, depolarization measurements on a random sample yield only one ratio involving α_x, α_y, and α_z, while depolarization measurements on an ordered sample yields three ratios.

D.   Two-Photon Absorption

Simultaneous absorption of two different photons is governed by the formula[9]

$$I(\omega,\theta,\phi) = 8\pi^3\alpha^2\omega_1\omega_2 g(\omega_1+\omega_2)(\hat{v}_2 \cdot \underset{\approx}{S}_{mn} \cdot \hat{v}_1)^2, \qquad (57)$$

where α is the fine structure constant, ω_1 and ω_2 are the frequencies of the two photons whose polarizations are $\hat{v}_1$ and $\hat{v}_2$, $g(\omega)$ is the absorption lineshape function for the molecule, and $\underset{\approx}{S}_{mn}$ is the two photon absorption tensor. The elements of $\underset{\approx}{S}_{mn}$ are

$$(S_{ij})_{mn} = \underset{k}{\Sigma} \; [\; \frac{<m|r_i|k><k|r_j|n>}{\omega_{km} - \omega_1} + \frac{<m|r_j|k><k|r_i|n>}{\omega_{km} - \omega_2}]$$

$$(58)$$

McClain and Harris[9] have reviewed the theory of two-photon absorption in random systems. The parameters that enter are the elements of the absorption tensor. They used group theoretical arguments to list the irreducible tensor patterns of many types of molecules; these tensors contain from one to nine different elements. In a partially ordered sample, the elements of the irreducible absorption tensor will still be parameters, and three new parameters will be the three Euler angles that relate the molecular axis system to the principal axis system of the irreducible absorption tensor. Conceptually, the type of information available in a two-photon absorption experiment is similar to that available in a Raman experiment.

V.   Discussion

The chief result of this paper is the derivation of $P(\theta,\phi,\omega,\underset{\sim}{\Delta})$ in equation (22); This result is an extension of the density of states theory introduced in reference 2. The two-vector density of states theory retains most of the advantages of the one-vector density of states theory, and these advantages are discussed at length in Paper I. Here, we will outline the major benefits afforded by adopting our approach to analyzing the results of spectroscopies governed by the response functions in Eqs. (3) and (4).

Previous approaches to orientation averaging have introduced a distribution function $P'(\theta',\phi',\psi')$ which gives the probability that a member of the ensemble is related to the laboratory axis system by the Euler angles θ',ϕ', and ψ'. This distribution function is then expanded in terms of the Wigner rotation matrix elements[9,10]

$$P'(\theta',\phi',\psi') = \sum_{\ell mn} P_{\ell mn} \mathcal{D}^{\ell}_{mn}(\theta',\phi',\psi') \qquad (59)$$

where $P_{\ell mn}$ are the ℓmn^{th} moments of the distribution function defined by

$$P_{\ell mn} = \frac{2\ell+1}{8\pi^2} \int_0^{2\pi} \int_{-1}^{1} \int_0^{2\pi} \mathcal{D}^{\ell}_{mn}(\theta',\phi',\psi') P'(\theta',\phi',\psi')$$

$$\times \; d\phi' d\cos\theta' d\psi' \qquad (60)$$

When Equation (59) is substituted into orientational averaging formulas with the response functions in Eqs. (3) and (4), the results are expressions that depend only on the $\ell = 2$ and $\ell = 4$ moments, and the structural parameters inherent in the type of spectroscopy analyzed (e.g. for fluorescence polarization, the expressions depend on the $\ell = 2$ and $\ell = 4$ moments, z_1, z_2 and ϵ).

There are two basic problems with the Wigner expansion approach:

(1) If one knows the spectroscopically inherent structural parameters, it is possible to probe the distribution function with an experiment on a partially ordered sample. In the Wigner expansion approach, this experiment can yield only the $\ell = 2$ and $\ell = 4$ moments, and these moments may be of little value in describing the distribution function, especially if the expansion in equation (59) is slowly convergent. The best one can do is to construct a model for the system, calculate $P'(\theta', \phi', \psi')$, and see if calculated moments from Eq. (60) agree with the measured moments. However, no general method for constructing $P'(\theta', \phi', \psi')$ from a model that involves a rotation scheme of four or more rotations has been described.

(2) If one wishes to measure the spectroscopically inherent structural parameters, it is necessary to know the $\ell = 2$ and $\ell = 4$ moments, or at least to be able to place limits on the moments. Because $P_{\ell mn}$ are merely mathematical projections of the unknown distribution function on the Wigner

rotation matrix elements, there is no justification for placing limits on the moments.

The density of states approach overcomes these problems. One way to think of the difference between our approach and the Wigner expansion approach is that we represent the distribution function in terms of the order parameter $\underset{\sim}{\Delta}$ instead of the $P_{\ell mn}$ moments. The major benefits afforded by adopting our approach are:

(1) If one uses known spectroscopically inherent structural parameters to probe the distribution function, one may obtain $\underset{\sim}{\Delta}$. The $\underset{\sim}{\Delta}$ parameter gives a better definition of the distribution function. In fact, one could find all the $P_{\ell mn}$ moments from $\underset{\sim}{\Delta}$ by an equation

$$P_{\ell mn} = \iiint \mathcal{D}^{\ell}_{mn}(\theta',\phi',\psi')F(\theta',\phi',\psi',\underset{\sim}{\Delta})d\theta'd\phi'd\psi' \quad (61)$$

where $F(\theta',\phi',\psi',\underset{\sim}{\Delta})$ is a distribution function which could be derived from $P(\theta,\phi,\psi,\underset{\sim}{\Delta})$ by converting from the molecular axis system to the laboratory axis system. Furthermore, each Λ_i is related to some physical property of the ensemble and, as such, is a quantity of interest.[1]

(2) If one wishes to measure the spectroscopically inherent structural parameters, it is necessary to place limits on $\underset{\sim}{\Delta}$. This is easier than placing limits on the moments, because $\underset{\sim}{\Delta}$ may often be restricted from physical considerations.

(3) $P(\theta,\phi,\omega,\underset{\sim}{\Delta})$ is evaluated from a model for the system which is defined by the rotations $R_1(\alpha_1) \ldots R_n(\alpha_n)$ and the weighting functions $g_1(\alpha_1) \ldots g_n(\alpha_n)$. As such, it is straightforward to interpret data in light of a specific model.

(4) The fact that we average orientations in a molecular axis system, instead of a laboratory axis system, sometimes makes our approach more efficient. For example, reference 4 gives an example of a system where the distribution function is axially symmetric in the molecular axis system but not in the laboratory axis system.

Most experimental work involving two-vector problems has been done on random systems. Work on partially ordered systems has either resorted to the cumbersome expansion method[11-13] or been analyzed only qualitatively.[14] As a result, experimental studies of two-vector spectroscopies on partially ordered systems is probably an underexplored area. It can serve as a valuable probe to structural features such as the orientation of transition moments in the molecular axis system and the principal axis system. In closing, we note that two-vector spectroscopies having response functions other than Eqs. (3) and (4) can still be analyzed by our approach, with Eq. (2) serving as a starting point for such an analysis.

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FIGURE CAPTIONS

1. Definition of the angles θ, ϕ, and ω in the molecular axis system. θ and ϕ are the traditional spherical angles for the vector $\hat{v}_1'$; θ is the polar angle and ϕ is the azimuthal angle. ω is the angle between $\hat{v}_2'$ and an arbitrary (but fixed) vector in the plane perpendicular to $\hat{v}_1'$.

2. Experimental set-up for a polarization experiment with exciting light polarized along the z axis. The axis system shown is the laboratory axis system.

3. Experimental set-up for a polarization experiment with exciting light polarized along the x axis. The axis system shown is the laboratory axis system.

TABLE LEGEND

1.   The functional forms of $\alpha_2(\theta,\omega)$ and $\alpha_3(\theta,\omega)$ in Eq. (23).

When a $\pm$ appears in an equation for $\alpha_2(\theta,\omega)$ or $\alpha_3(\theta,\omega)$, both terms must
be included; i.e. $P(\theta,\omega) = \sin\theta\{G[\alpha_2^+(\theta,\omega),\alpha_3^+(\theta,\omega)] + G[\alpha_2^-(\theta,\omega),$

$\alpha_3^-(\theta,\omega)]\}$

TABLE I

RS[a]	$\hat{v}_1$	$\hat{v}_2$	$\alpha_2(\theta,\omega)$	$\alpha_3(\theta,\omega)$[b]	$\alpha_3(\theta,\omega)$[c]
ZYZ	$(\cos\psi,\sin\psi,0)$	$(0,0,1)$	$\cos^{-1}(\sin\theta\cos\omega)$	$\psi-\cos^{-1}(\pm\cos\theta/\sin\alpha_2)$	0^d
ZYZ	$(\cos\psi,0,\sin\psi)$	$(0,1,0)$	$\cos^{-1}(\cos\theta\sin\psi\pm\cos\psi\sin\theta\sin\omega)$	$\sin^{-1}(\sin\theta\cos\omega/\sin\alpha_2)$	$\frac{\pi}{2}-\omega$
ZYZ	$(0,\cos\psi,\sin\psi)$	$(1,0,0)$	$\cos^{-1}(\cos\theta\sin\psi\pm\cos\psi\sin\theta\sin\omega)$	$\cos^{-1}(\sin\theta\cos\omega/\sin\alpha_2)$	ω
ZYZ	$(0,0,1)$	$(\cos\psi,\sin\psi,0)$	θ	$\psi\pm\omega$	$\psi\pm\omega$
ZYZ	$(0,1,0)$	$(\cos\psi,0,\sin\psi)$	$\cos^{-1}(\sin\theta\sin(\psi\pm\omega))$	$\sin^{-1}(\cos\theta/\sin\alpha_2)$	0^d
ZYZ	$(1,0,0)$	$(0,\cos\psi,\sin\psi)$	$\cos^{-1}(\sin\theta\sin(\psi\pm\omega))$	$\cos^{-1}(\cos\theta/\sin\alpha_2)$	0^d
ZXY	$(\cos\psi,\sin\psi,0)$	$(0,0,1)$	$\sin^{-1}(\cos\theta\sin\psi\pm\cos\psi\sin\theta\sin\omega)$	$\cos^{-1}(\sin\theta\cos\omega/\cos\alpha_2)$	ω
ZXY	$(\cos\psi,0,\sin\psi)$	$(0,1,0)$	$\sin^{-1}(\sin\theta\cos\omega)$	$\psi-\sin^{-1}(\pm\cos\theta/\cos\alpha_2)$	0^d
ZXY	$(0,\cos\psi,\sin\psi)$	$(1,0,0)$	$\sin^{-1}(\cos\theta\cos\psi\pm\sin\psi\sin\theta\sin\omega)$	$\sin^{-1}(\sin\theta\cos\omega/\cos\alpha_2)$	$\frac{\pi}{2}-\omega$
ZXY	$(0,0,1)$	$(\cos\psi,\sin\psi,0)$	$\sin^{-1}(\sin\theta\sin(\psi\pm\omega))$	$\cos^{-1}(\cos\theta/\cos\alpha_2)$	0^d
ZXY	$(0,1,0)$	$(\cos\psi,0,\sin\psi)$	$\frac{\pi}{2}-\theta$	$\frac{\pi}{2}-\psi\pm\omega$	$\frac{\pi}{2}-\psi\pm\omega$
ZXY	$(1,0,0)$	$(0,\cos\psi,\sin\psi)$	$\sin^{-1}(\sin\theta\cos(\psi\pm\omega))$	$\sin^{-1}(\cos\theta/\cos\beta)$	0^d

[a] Rotation scheme or the order and axes of three rotations required to generate the ensemble.

[b] Use these formulas if the denominators are not equal to zero.

[c] Use these formulas if the denominators in the previous column equal zero.

[d] In these cases, any value of α_3 can be used because for any physically realizable model, $G[\alpha_2,\alpha_3]$ will be independent of α_3 when the denominators in the previous column equal zero.
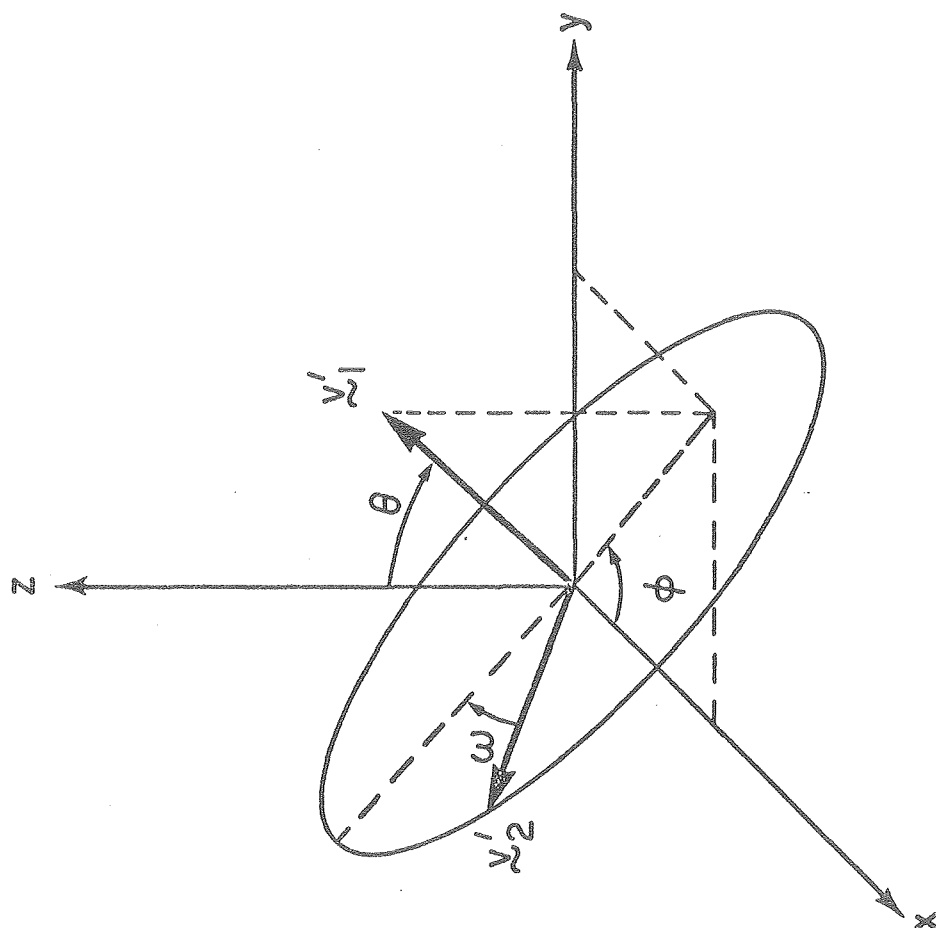
FIGURE 1
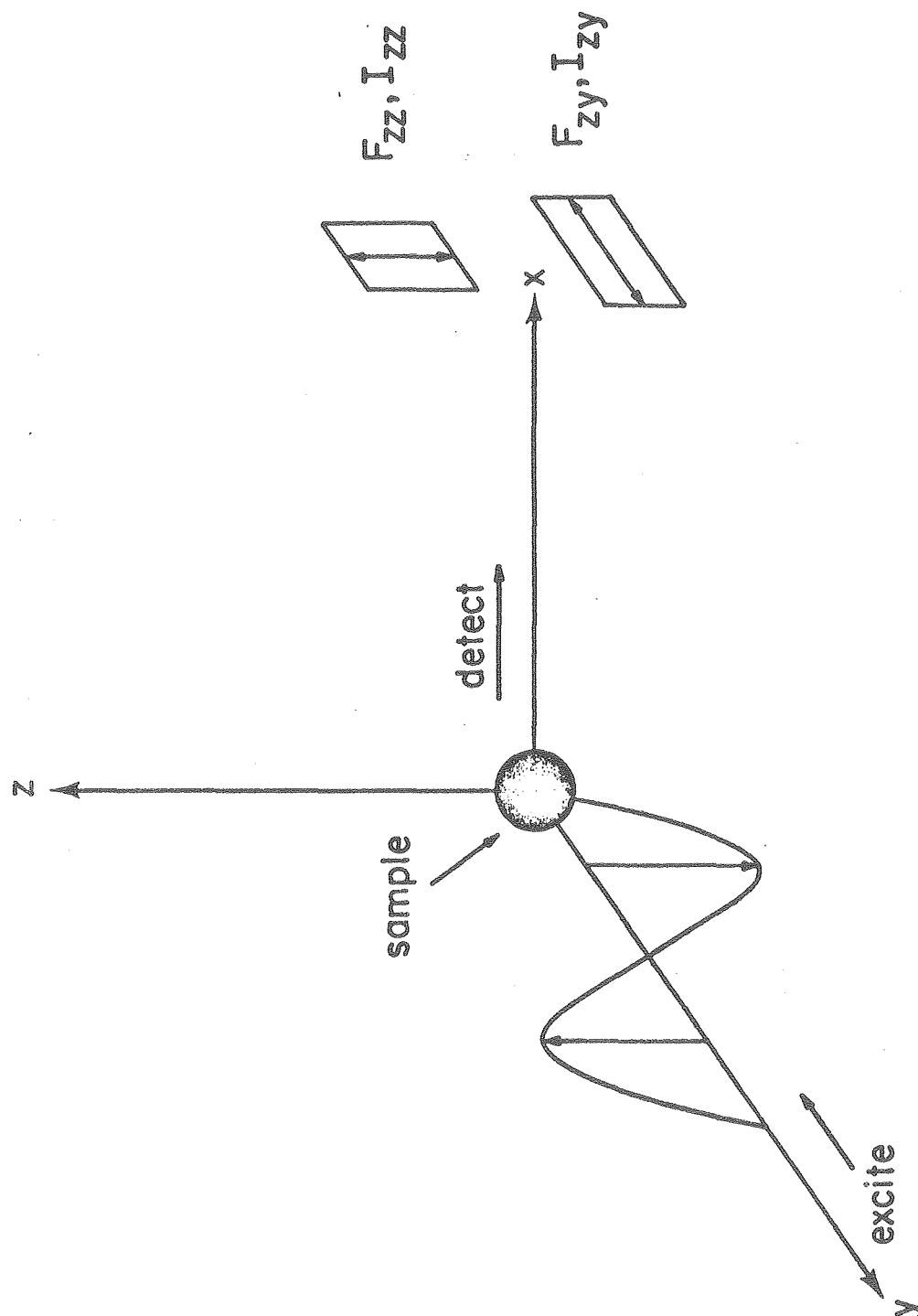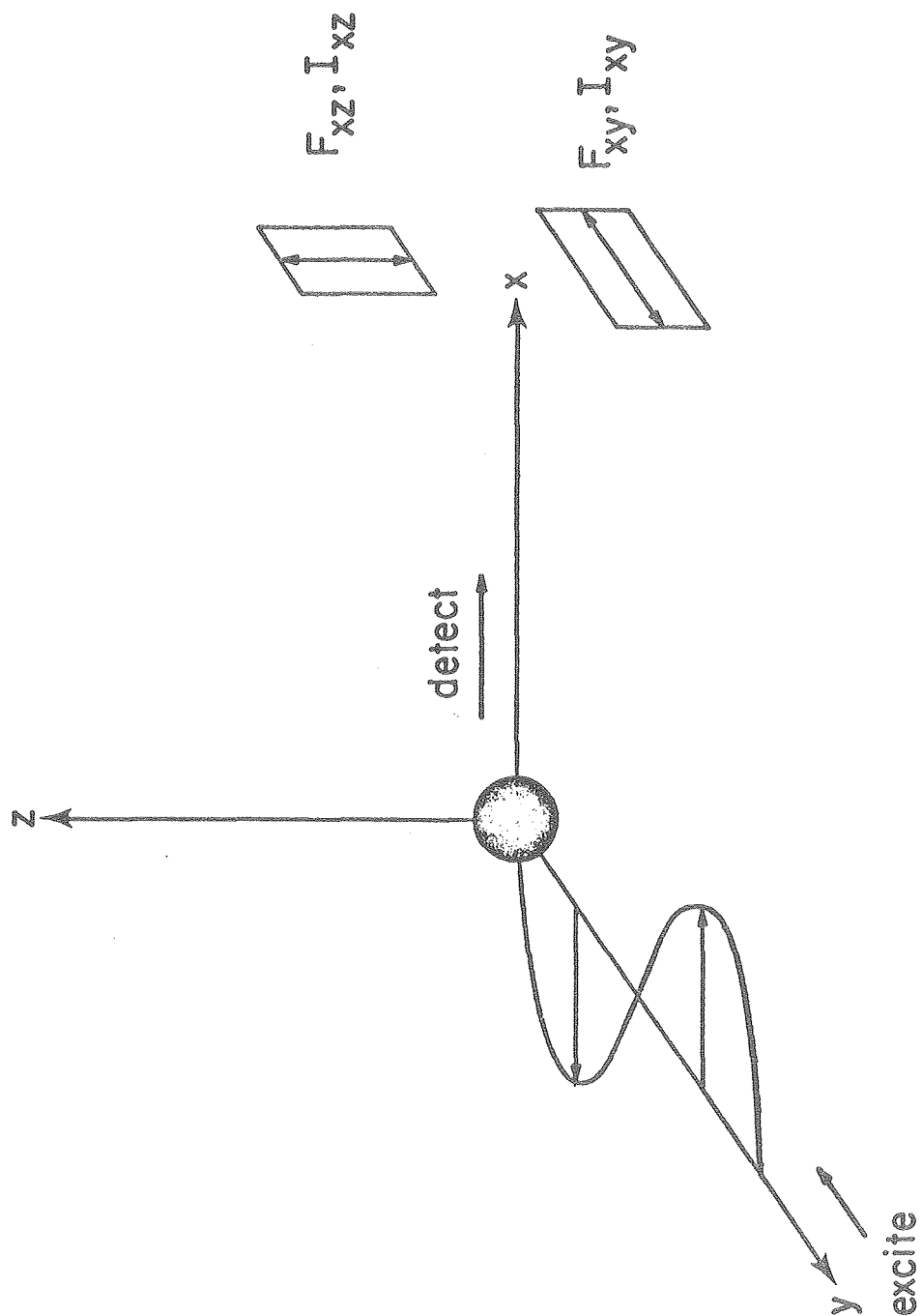
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F_{zz}, I_{zz}

F_{zy}, I_{zy}

x

detect

z

sample

excite

y

FIGURE 2

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FIGURE 3

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